"STUDY OF THE GROWTH, BY SOLID STATE RECRYSTALLIZATION, AND ASSESSMENT OF ZNSE CRYSTALS AS SUBSTRATES FOR BLUE EMITTING DEVICES"

Final Technical Report

by

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Abstract : For a better understanding and control, the process of solid state recrystallization of ZnSe is studied through the different aspects of growth kinetics, influence of residual impurities on the kinetics, 'initial texture/orientation of the growing crystals' relationship, twinning issue, determination of the vacancy concentration, and doping. An activation energy of ~ 400 kJ/mole is determined for the migration of the grain boundaries at the early stage of the growth under both Zn- and Se-rich conditions. Like in the case of metals, a law of the form $D = kt^{1/n}$ is found between the grain diameter D and the time t, $1/n$ being respectively about 0.25 and 0.1 under Se-rich and Zn-rich conditions. The presence in the source of residual donors such as Al, In and Cl is found to inhibit the SSR grain growth. Preferential orientations (111), (311) and (220) found by X-ray diffraction in the initial CVD samples are progressively left, and growth directions around (110) are found to be favored. The presence of twins in most of the initial micrograins, as found from electron microscopy observations, is supposed at the origin of twinning frequently observed in the crystals. The size and quality of the SSR crystals are found to depend on orientation and size factors of the initial samples. The dislocation density of the SSR crystals is estimated to be $\leq 10^2 \, cm^{-2}$. A vacancies concentration of some $10^{19} \, cm^{-3}$ is estimated on both sides of stoichiometry, assuming a vacancy model to be valid, from lattice parameters measurements. Using Al diffusion, conductive ($8 \times 10^{-2} \, \Omega.cm$) n-type crystals with carrier concentrations up to $5 \times 10^{17} \, cm^{-3}$ and electron mobilities about 200 cm^2/Vs at room temperature are obtained.

Keywords : ZnSe, solid state recrystallization, growth kinetics, twinning, stoichiometry, doping, electron microscopy study, X-ray diffraction measurements.

1. Statement of the work.

Let us first recall the general objectives and scope of the work.

The aim is to study the process of solid state recrystallization of ZnSe at a microscopic scale with the dual objectives of allowing better control of the growth conditions with the resulting improvement of crystalline quality, and furthering the fundamental understanding of solid state recrystallization.

An additional objective of this project was to establish cooperative working relationship with Army researchers.

The scope of the work was that at a macroscopic scale, the growth kinetics should be studied as a function of the growth conditions, i.e. nature of the atmosphere surrounding the crystals, partial and total pressures, temperature, time. Size and shape of grains should be determined by cathodoluminescence imaging in a scanning electron microscope (SEM). A fine analysis of the texture by X-ray diffraction in the reflection-transmission mode should be achieved. The thermodynamic constants of the growth process should then be determined from these measurements.

At a microscopic scale, using conventional transmission electron microscope (TEM), the structure and evolution of dislocations and grain boundaries, and their interaction with point defects, either native or extrinsic (impurities) should be studied. From the results of this experimental investigation, a theoretical simulation of the growth should be started.

Furthermore, doping experiments should be undertaken, in order to obtain conductive substrates suitable for achieving backside injecting electrical contacts. These doping

experiments should be carried out by diffusion from a vapour phase either during the SSR annealing or post SSR, according to the influence of extrinsic defects introduced in the lattice on the SSR kinetics.

At each step of the growth process, the crystals should be submitted to structural and electronic assessment, in close relationship with the ARL-Sensors Directorate.

This final report will follow the above scope, and address successively the growth kinetics, the influence of residual impurities on the kinetics, the 'initial texture/orientation of the growing crystals' relationship, the twinning issue, the determination of the vacancy concentration in ZnSe, the doping.

2. Growth kinetics

The primary stage of recrystallization, which consists in dislocations migration and rearrangement giving a new microstructure, occurs in a highly deformed material. Our ZnSe scraps are CVD grown without any cold work during the process so that only the second stage of rerystallization, i.e. grain growth, is involved.

A simple model has been used to calculate the activation energy of the grain boundaries migration. According to this model, the boundary migration rate is expressed by the product of its mobility (m) by its driving force (f_m), according to :

$$V_m = m.f_m$$

The mobility of the grain boundaries obeys such an Arrhenius law as:

$$m = m_0. \exp\left(-\frac{Q_m}{RT}\right)$$

where R is the Gas Constant, Q_m is the activation energy of the grain boundaries migration, m_0 is a constant, T is the temperature.

From Burke and Turnbull [1], the recrystallization rate can be expressed as :

$$\frac{dR}{dt} = \frac{m\gamma}{R}$$

where R is the mean radius of the grains and γ is the energy of the grain boundary.

By integration of this equation, it comes : $R^2(t) - R_0^2 = m\gamma t$, R_0 being the mean radius of the grains at t = 0.

If $R_0 \ll R$, one obtains $R \approx m\gamma t^{1/2}$ which relates to the more general empirical expression $R \approx m\gamma^{1/n}$, with 1/n lying in the 0.25 - 0.5 range for pure metals.

In order to study the ZnSe SSR growth kinetics, a first set of experiments have been achieved under Se and Zn partial pressures at three growth temperatures, 650, 820 and 950 °C and, for each temperature, at three growth times, 7, 14 and 21 days.

The mean area of the grains has been determined using a microscope; the mean radius $\bar{R}$ has been deduced assuming this area to be a circle. $\bar{R}^2(t) - \bar{R}_0^2 = f(t)$ has been plotted for each temperature T_i, t being the recrystallization time.

The slopes P_i give $m_i\gamma_i$, and Q_m can then be extracted from the Arrhenius plot of the expression :

$$m_i\gamma_i = m_0\gamma_i \cdot \exp\left(-\frac{Q_m}{RT}\right)$$

A value close to $Q_m \sim 400$ kJ/mole has been determined at 950°C under both Zn and Se partial pressures at the early stage of the growth. But it was found that some dispersion occurred according to the starting samples used. It appeared that it was absolutely necessary to use samples extracted from a same scrap to obtain reproducible and comparable results. As will be shown later, the presence of residual impurities can deeply alter the results. Consequently, given also the lack of precision of the grain radii determination and the simplicity of the model, this value of 400 kJ/mole, similar under both Zn- and Se-rich conditions, has to be considered as a very rough estimation. That is why a second set of more controlled experiments has been undertaken.

A second set of annealing runs during different times, ranging from 16 hours to three weeks, either under Zn (1.2 atm) or Se (5 atm) atmospheres, have been achieved to perform a more precise kinetics study. The samples, extracted from the same scrap, were heated up to 1273 K (in 4 hours), kept at this temperature during 16, 48, 144 and 430 hours, and cooled down to room temperature (in 48 hours). After polishing and chemical etching with a 30% sodium hydroxide boiling solution, the microstructure was revealed. The mean area of the grains has been measured by scanning electron microscopy and optical microscopy ; the mean radius was then deduced assuming this area to be a circle. The results are presented in figure 1, for the annealing under Zn pressure, and figure 2, for the annealing under Se pressure. The diameter of the grains vary as $D = 0.86t^{0.24}$ for the Se-rich growth conditions and $D = 1.65t^{0.06}$ for the Zn-rich growth conditions. Such laws $D = f(t^{1/n})$ are commonly found in the case of metals, as indicated above, where the inverse of the grain growth exponent n lies in the range 0.1 - 0.5 [2]. In order to determine the activation energies associated with the growth process, other sets of experiments are now necessary for at least two different temperatures. Note that such experiments are extremely time consuming.

The microstructure of the samples grown under Zn partial pressure appears much more defective than the one of samples grown under Se partial pressure, as shown in figure 3. Etch pits on the (111) planes indicate also than the dislocation rate may be a hundred times more elevated in the Zn-rich samples.

3. Influence of residual impurities on the SSR kinetics

As already pointed out in the case of metals, residual impurities can heavily inhibit the boundary movements. As an example, according to Lücke et al. [3] 0.01 weight per cent manganese in aluminium can lower the boundary mobility to 10^{-11} of its value in the pure metal. ZnSe SSR growth rates considerably lower than usually observed have been obtained with
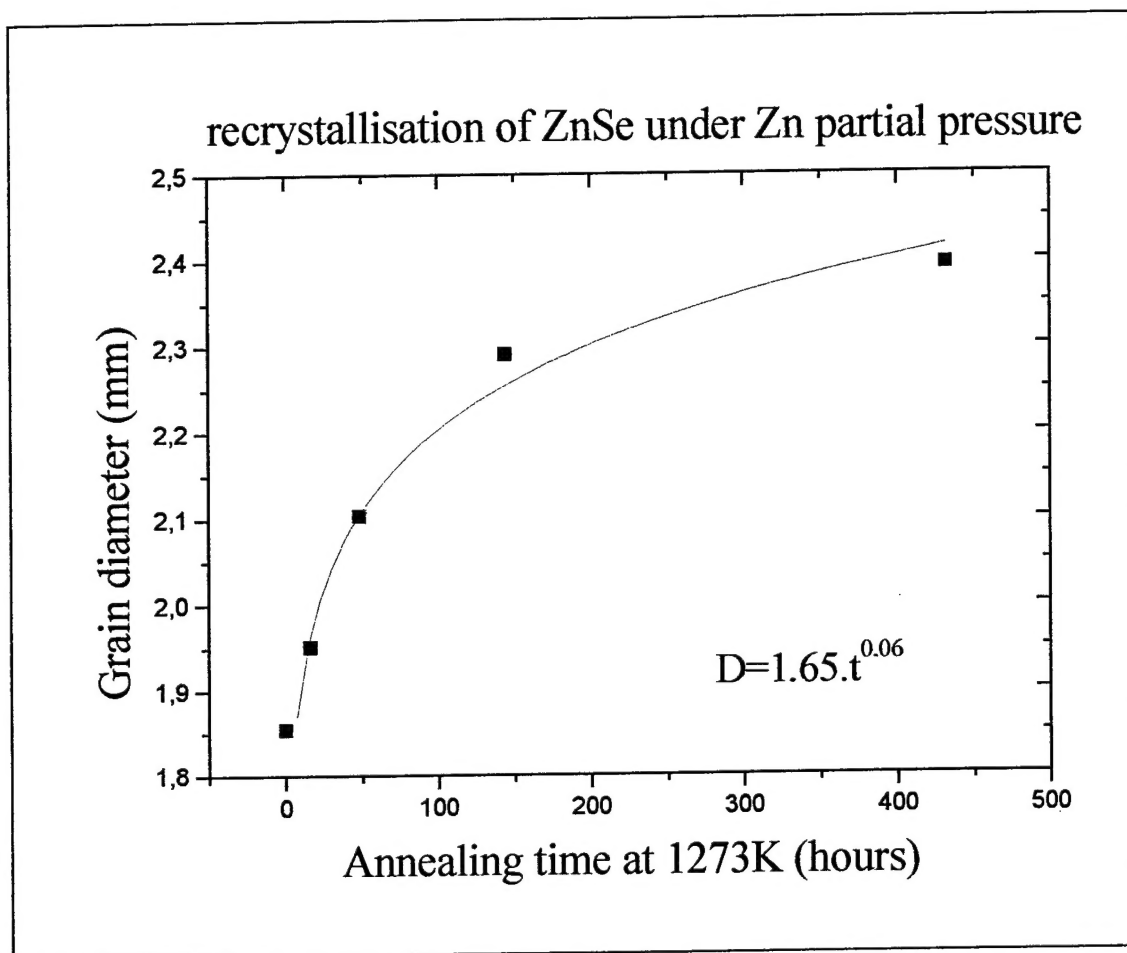
Figure 1

recrystallisation of ZnSe under Se partial pressure

Grain diameter (mm) vs Annealing time at 1273K (hours)
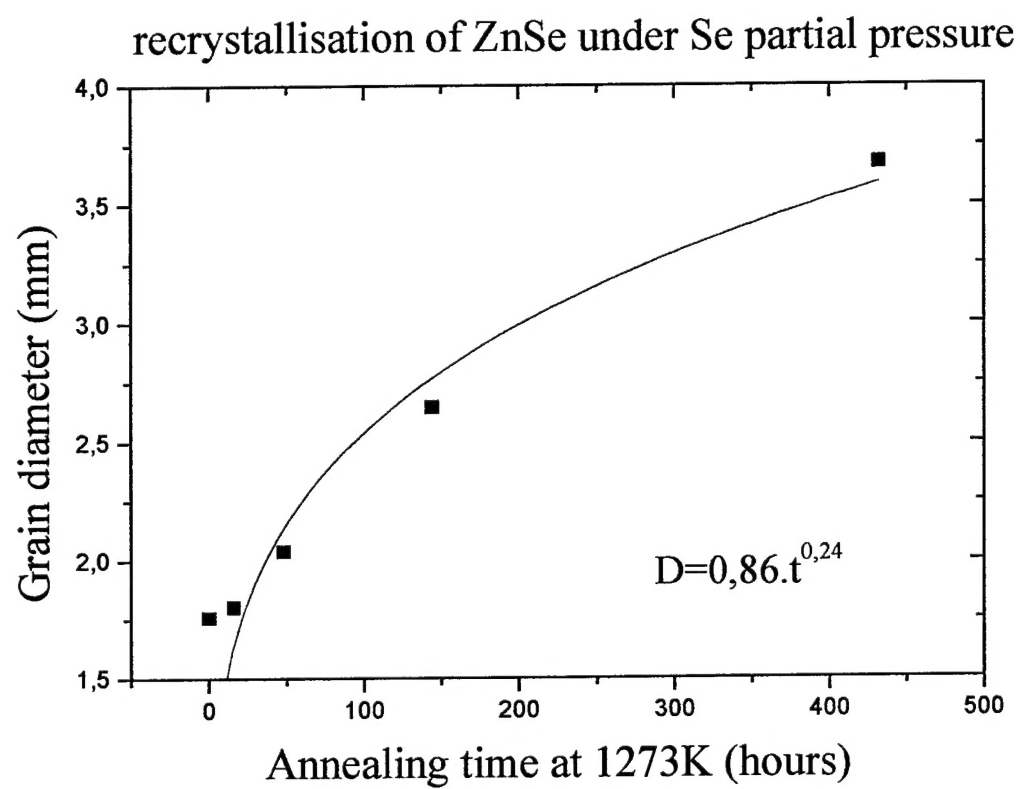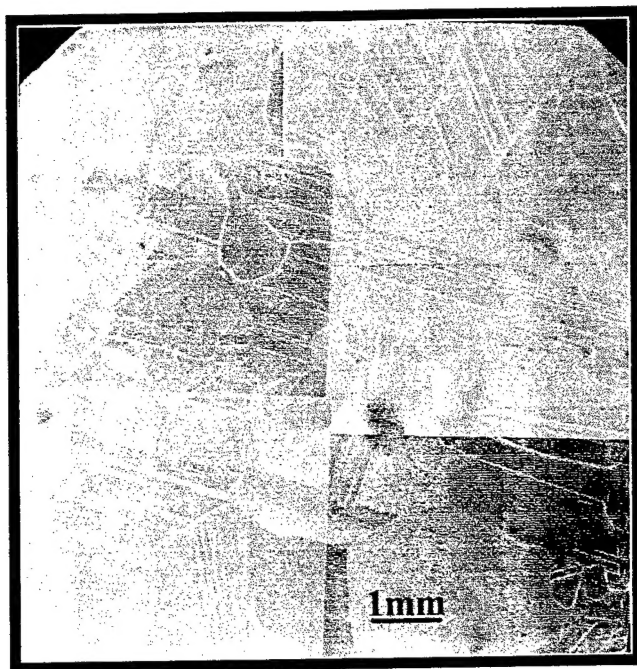
$D = 0{,}86.t^{0{,}24}$
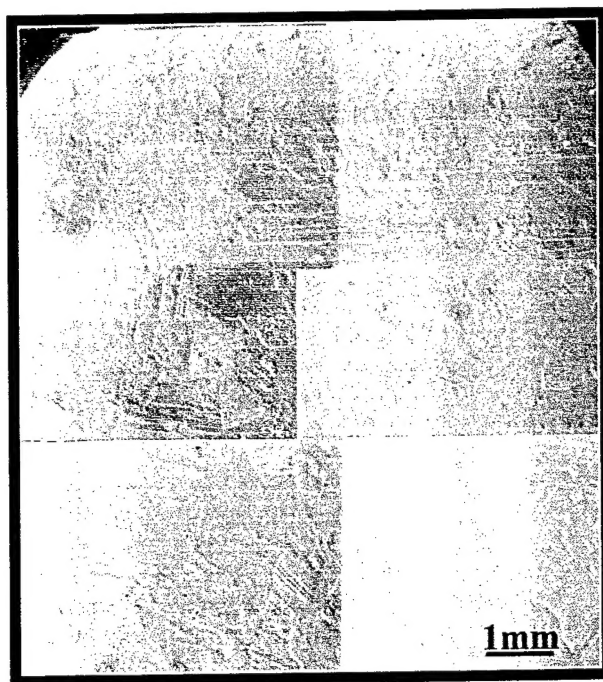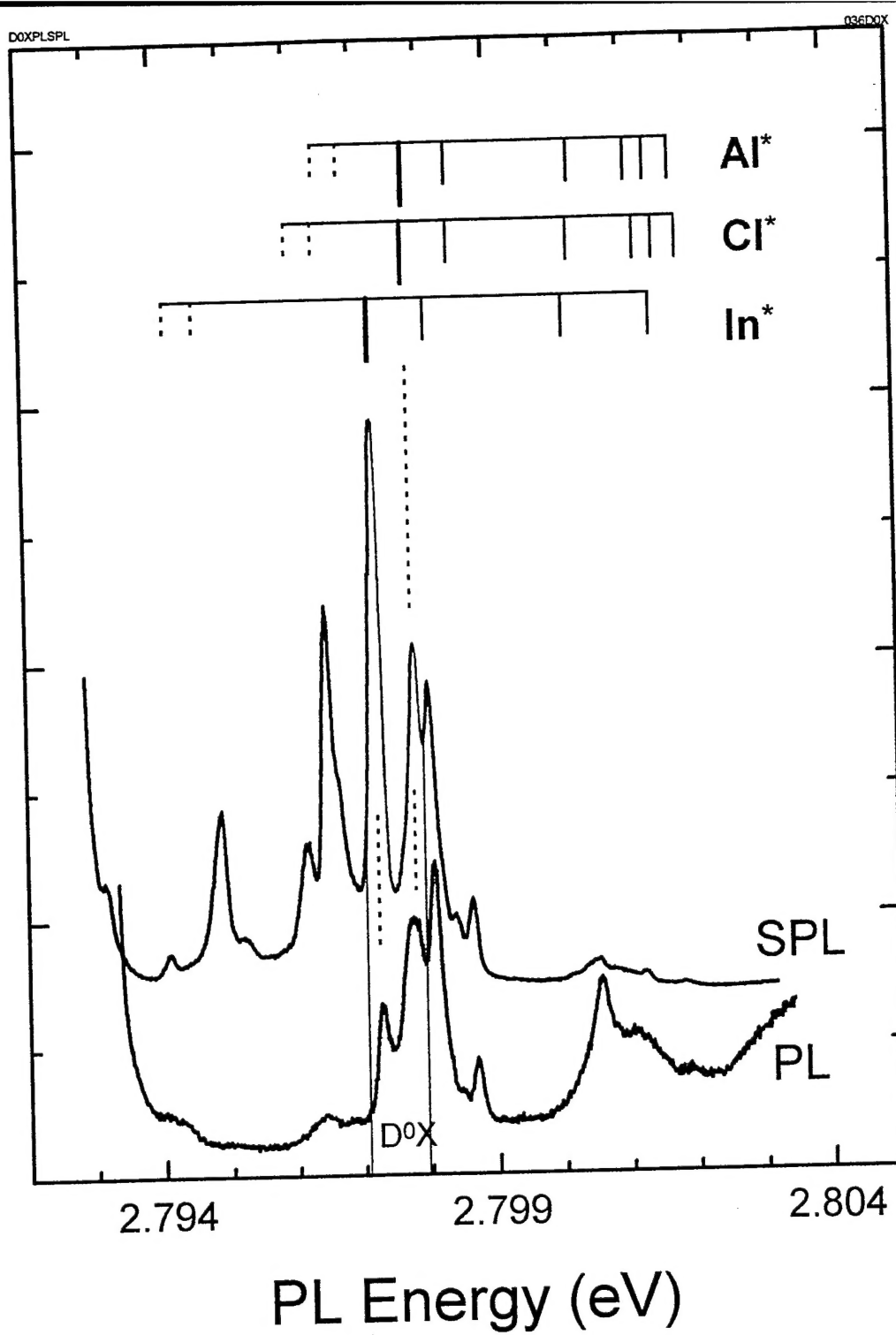
Figure 2

Sample annealed under Se partial pressure (5 atm)

Sample annealed under Zn partial pressure (1 atm)

Figure 3.

*After Isshiki *et al*, PR B **36**, 2568 (1987)

Figure 4

some starting samples labelled B, extracted from some ZnSe scraps. Crystals of only some mm^3 in size were obtained when using such starting material B under conditions leading generally to single crystals of several cm^3, which roughly corresponds to growth rates more than 10^3 slower for material B.

By comparison with the spectra reported in ref. [4] for very pure starting material giving rise to high SSR growth rates, photoluminescence spectra (PL) measured at 2K of source samples B have been found to present additional D^{0}X lines, as shown in figure 4. These lines can be attributed, according to Isshiki et al. [5], to residual donors. Al, Cl and In have then been identified in the spectra as residual impurities present together in samples B.

In figure 4 is also displayed a spectrum measured under a selective excitation (SPL) corresponding to the energy of the free exciton with n = 2. This spectrum shows emission lines associated with the fundamental and excited states of D^{0}X and the I$_3$ lines of the three impurities. The assignment of the PL lines is also supported by resonant Raman scattering experiments showing distinctly the 2s and 2p states emissions of these three impurities.

To summarize, the presence in the CVD source samples of residual donors such as Al, In and Cl inhibit the ZnSe grain growth during the recrystallization process. The purity of the CVD source is a deciding parameter to succeed in the ZnSe SSR growth.

4. Initial texture/orientation of the growing crystals relationship

The initial texture of the microcrystalline CVD grown source material used for SSR experiments has been studied by X-ray diffraction. Pole figures, an example of which is given in figure 5, as well as X-ray diffraction patterns (figure 6) indicate (111), (311) and (220) as preferential orientations. In polycrystalline ZnSe layers grown by low-pressure CVD, Hartmann et al. have found (111), (422) and (331) as preferential growth directions [6]. We have further studied from the diffraction patterns the evolution of the growth directions as a function of the SPR annealing time and pressure conditions. It turns out that the statistical determination of the preferential directions becomes more and more uncertain with the reduction of the number of grains. Nevertheless, the initial preferential directions are progressively left, and growth directions around (110) have been found to be favored.

Following the statistic determination of the preferential orientations presented by the initial microcrystalline samples and of their evolution during the growth process, we have carried out a study of the texture at microscopic scale by electron microscopy. First TEM experiments have been achieved on two kinds of material located at the two "boundaries" of the SSR experiments, the microcrystalline CVD grown source material, and SSR grown single crystals. The samples have been first studied by scanning electron microscopy. After suitable thinning and chemical etching, the microcrystalline CVD grown samples provided by II-VI Inc. show grain sizes comprised between 10 and 80 µm (observations achieved in cathodoluminescence mode). A great majority of the grains are highly twinned. The twinning planes cross the grains either partially or totally. In case of only partially crossing, several twinning plane orientations can cohabit. Samples with the observation plane either parallel or perpendicular to the CVD growth plane have been compared. In the first case, the grain size is statistically slightly higher. The material has been then found to present some microstructural anisotropy due to the mode of CVD growth.

In agreement with these observations, different behaviors have been found during the SSR experiments depending on the orientation of the parallelepiped source samples. Parallelepiped samples have been cut either with their longitudinal axis perpendicular to the ZnSe CVD scraps growth direction (samples labeled ⊥), or parallel to the scraps growth direction (samples labeled //). Larger crystals are obtained from samples labeled ⊥.
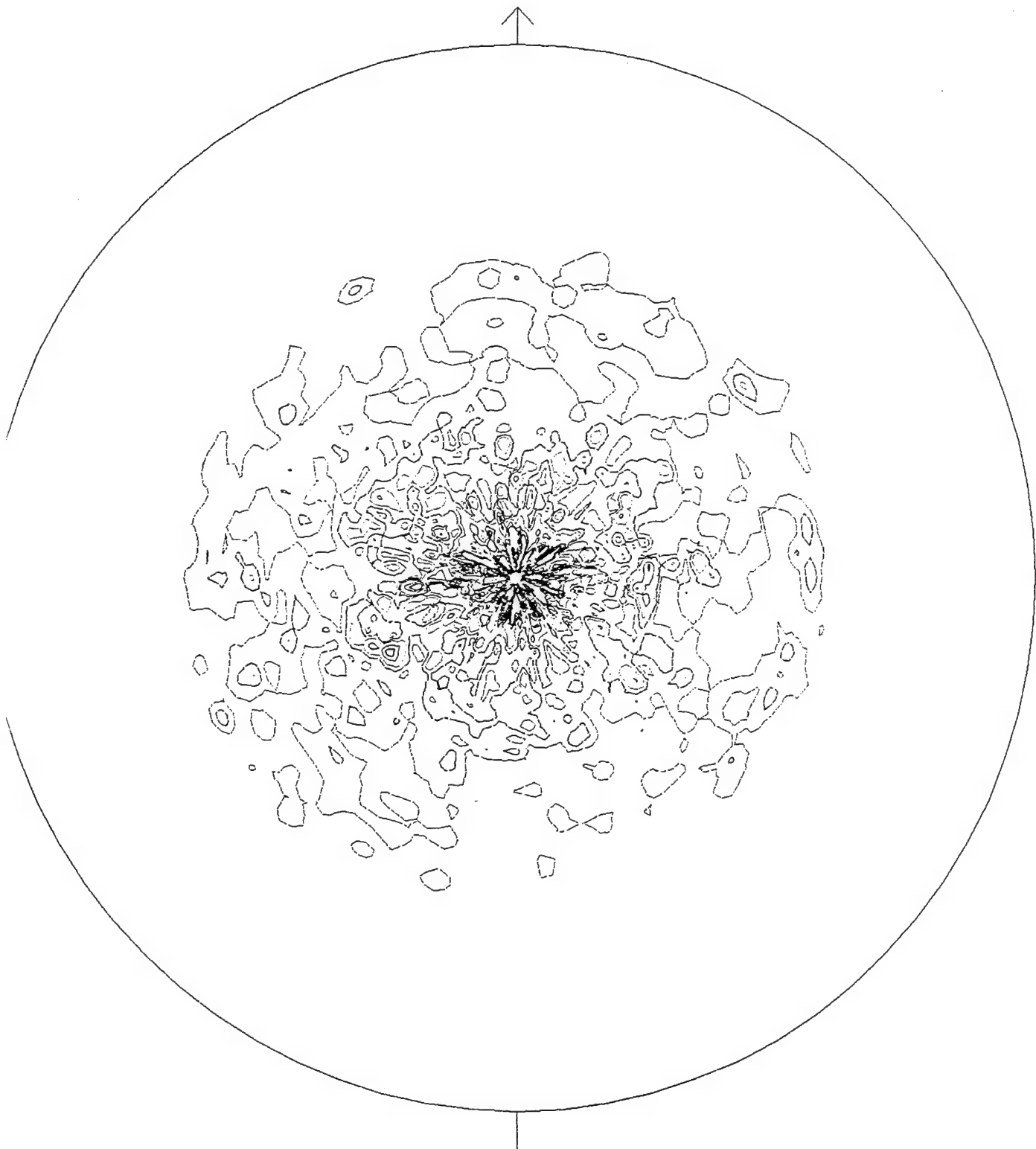
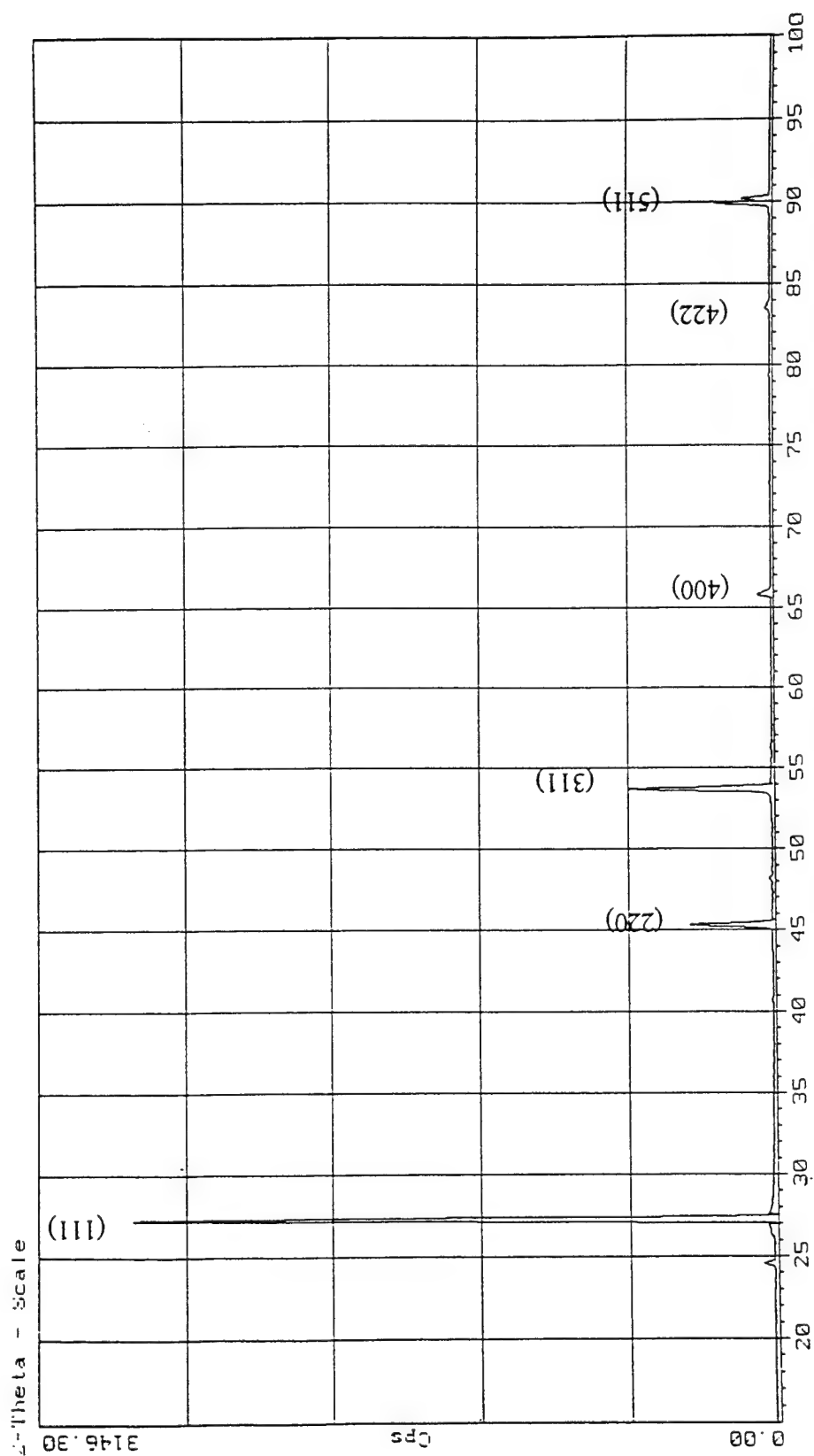Pole figure : 111

Figure 5

Figure 6

We have noticed as well that the size of the crystals obtained from SSR experiments, for identical growth conditions, was all the larger since the size of the initial samples was large. The migrating boundaries disappear at the important places constituted by samples faces, whose morphology highly conditions the SSR results as well.

After mechanical thinning, chemical etching and ion milling, the microcrystalline samples have been observed by transmission electron microscopy. The high tendency to twinning of the micrograins is confirmed : microtwins series with a distance of the twin planes of less than 100 nm are observed.

Chemical analysis by EDX of the samples reveals the presence of Zn, Se, Cu and O. The concentration of O is very small and could be due to the presence of a very thin oxide layer created during the chemical etching. The Cu content could be attributed to the fact that the X fluorescence of Se excites the Cu atoms constituting the sample holder or included in the microscope column. A Se composition systematically in excess (in between 50.4 et 53.6 % at. over four measurements) has been measured. Because of the previous remark concerning copper, the Se/Zn composition given above has to be considered only as a relative composition.

Finally, circular spots of diameter close to 100 nm have been observed as well. The E.D.X chemical analysis of these spots shows a high Se excess (60 to 70 % Se atoms over 3 measurements). These spots are essentially localized on the side of the slides, but some of them can be found also in the grain boundaries as well and even inside the grains. These zones with Se excess could be constituted during the preparation of the samples, because of some heating resulting from the ion milling process.

TEM observations of SSR grown single crystals has also been achieved. A very small concentration of dislocations has been found, i.e. no dislocation is frequently visible given the small studied area at the magnifications used. We estimate the dislocation density to be $\leq 10^2$ cm^{-2}, in agreement with the measurements achieved by X-ray diffraction imaging by D. Black from NIST on our crystals, using the synchrotron light source of Brookhaven National Laboratory.

5. Twinning

Twins are frequently found in the SSR grown ZnSe crystals, mainly in samples of parallelepiped shape presenting particular orientations of their longitudinal axis beside the source texture, confirming some orientation relationship between growing crystal and microcrystalline matrix. Recrystallization twins occur frequently in various materials of face centred cubic structure. They appear mostly in the form of narrow or broad bands with parallel straight boundaries. The electron microscopy observations have thrown new light on this twinning issue. It turns out that twins are already present in most of the initial micrograins. Following the evolution of the twins orientations from the initial micrograins to the single crystals, one can reasonably assume that twins develop during the SSR annealing. Depending on the grain that grows to the detriment of its surrounding neighbors, twins can be found or not in the resulting single crystals. This shows the random character of twinning.

This probable origin of twins explain why different attempts that have been made to overcome this problem were unsuccessful. Strain-anneal experiments have been achieved, either applying the strain before or during annealing. No significant improvement has been found when the samples were stressed with pressures up to 20 kg/cm^2, in contradiction with the process reported in reference [7].

6. Determination of the vacancy concentration in ZnSe

Given the significant role of native defects, either Se or Zn vacancies, in the ZnSe SSR growth, we have tried to estimate the vacancy concentration from lattice parameter measurements, using for non-stoichiometric ZnSe the simple vacancy model of Paufler and Schulze [8]. This model allows to calculate the vacancy concentration from the elastic constants of ZnSe, the ionic radii of the elements and the relative variation of lattice parameters $\Delta a/a_0$. The results of very accurate lattice parameters measurements by X-ray diffraction are displayed in table 1.

Table 1

ZnSe samples	a (nm)	$\Delta a/a_0$
CVD source	0.56700	1.7×10^{-3}
Se-rich sample	0.56704	1.6×10^{-3}
Zn-rich sample	0.56797	

Taking as reference a lattice parameter intermediate between the ones of the Se-rich and Zn-rich samples, a concentration of vacancies of some 10^{19} cm^{-3} can be estimated on both sides of stoichiometry, assuming the vacancy model to be valid. This result has obviously to be considered only as a very rough estimation of the vacancy concentration. Nevertheless, these results are qualitatively confirmed by EDX and ICPMS measurements indicating respectively a Se concentration between 50.4 and 53.6%, in the Se-rich samples, and of about ~ 55% in the CVD source, while a Zn concentration of ~ 50.2% has been found in the Zn-rich samples.

7. Doping

In order to obtain highly conductive n-type crystals required for a backside injecting contact on the substrates used for the ZnSe-based blue emitting structures, doping experiments have been achieved either by diffusion from a liquid or from the vapor phase. The column III and column VII donors diffuse sufficiently rapidly to prepare single crystals doped with these elements by diffusion. In- and Al-doped crystals have been prepared by diffusion from a Zn-In and Zn-Al liquid alloy according to the process already proposed in reference [9]. The crystals are immersed in an In-doped or Al-doped liquid Zn solution at temperatures close to 900 °C during several days. It has been found that the doping procedure could be carried out either on bulk crystals or on thin (1 - 2 mm) wafers. In both cases, the eventual damage resulting from the diffusion process will be evaluated by X-ray diffraction measurements. Highly conductive (8×10^{-2} $\Omega.cm$) n-type crystals have been obtained after annealing at about 1000 °C in molten Zn doped with 10% Al. Carrier concentrations ranging from 4×10^{14} cm^{-3} to 5×10^{17} cm^{-3} and electron mobilities ranging respectively from 400 to 200 cm^2/Vs at room temperature have been measured on such crystals.

A collaboration has been engaged concerning the diffusion in ZnSe with Prof. E.D. Jones of the University of Coventry, who will measure the diffusion coefficients from radiotracers experiments.

Concerning chlorine, attempts have been made to incorporate chlorine by diffusion during the SSR annealing. In such conditions, the recrystallization growth is totally inhibited by the presence of these foreign impurities, as noticed in paragraph 3. Single crystals have been

annealed at temperatures in the range 650 - 750 °C under Cl pressures ranging between 5 and 10 atmospheres. The Cl pressures are obtained from the decomposition of a suitable amount of $PtCl_4$ powder that decomposes at these temperatures. SIMS measurements on the crystals reveal the presence of chlorine at significant level throughout the crystals. The crystals submitted to subsequent annealing to increase the Cl electrical activation ratio do not show any significant increase of their initial low conductivity. The crystals used for these experiments were previously grown under Se-rich conditions. Cl atoms occupying Se sites, crystals previously annealed under Zn-rich conditions have to be used for a sufficiently high concentration of chlorine atoms to be incorporated in Se vacancies. Such experiments are in progress.

8. Conclusions, recommendations, prospects

In order to better control the process of solid state recrystallization of ZnSe, to improve the quality of the crystals and to further the fundamental understanding of SSR, this process has been studied through the different aspects of growth kinetics, influence of residual impurities on the kinetics, 'initial texture/orientation of the growing crystals' relationship, twinning issue, determination of the vacancy concentration in ZnSe, and doping.

From preliminary experiments, an activation energy of ~ 400 kJ/mole has been determined for the migration of the grain boundaries at the early stage of the growth under both Zn- and Se-rich conditions. From a second set of better controlled experiments, a law of the form $D = kt^{1/n}$, like in the case of metals, has been found between the grain diameter D and the time t, the value of $1/n$ being respectively about 0.25 and 0.1 under Se-rich and Zn-rich conditions.

The presence in the source of residual donors such as Al, In and Cl, as identified from photoluminescence and Raman scattering measurements, has been found to inhibit the SSR grain growth.

Preferential directions (111), (311) and (220) found by X-ray diffraction measurements in the initial CVD samples have been shown to be progressively left, and growth directions around (110) have been found to be favored during the SSR process.

The presence of twins in most of the initial micrograins, as found from electron microscopy observations, has been supposed to be the origin of twinning frequently observed in the crystals.

The size and quality of the SSR crystals have been found to depend on the orientation of the initial samples used in the SSR experiments beside the texture of the CVD scrap matrix and on a size factor of the initial samples : the crystals have been found all the larger since the size of the initial samples was large.

The dislocation density of the SSR crystals has been estimated to be $\leq 10^2$ cm^{-2}.with rocking-curve FWHM about 15 arc.sec.

A vacancy concentration of some 10^{19} cm^{-3} has been estimated on both sides of stoichiometry from lattice parameters measurements by X-ray diffraction, assuming a vacancy model to be valid.

Finally, using Al diffusion at 1000 °C from a liquid Zn+10% Al alloy, conductive (8×10^{-2} Ω.cm) n-type crystals with carrier concentrations up to 5×10^{17} cm^{-3} and electron mobilities about 200 cm^2/Vs at room temperature have been obtained.

Several aspects of the work are still to be addressed or completed to get a good understanding and control of the SSR process. The growth kinetics has to be completed at two temperatures different from the one used so far. The results will then allow to tackle the grain

growth simulation. To solve the twinning issue, different unsuccessful attempts have been made so far, mainly by strain-anneal experiments, applying the strain before or during annealing. We think of applying either a magnetic or an electric field to the crystal during the SSR growth to try to "align" the Zn-Se dipoles that result from the highly ionic Zn-Se chemical bond. It should be moreover simpler to achieve the ZnSe growth by solid state epitaxy, using twin-free SSR grown ZnSe substrates and classical CVD grown samples as source. Twinning issue and orientation choice should be solved at the same time. Doping remains to be optimized, mainly concerning Cl doping. We will try to reach higher electron concentrations using Al doping. The incidence of doping on the structural quality of the crystals remains still to be evaluated.

Measurements on the ZnSe crystals we have provided to our U.S. partners are in progress (Dr J. Zavada, Research Triangle Park). This collaboration, highly contractually encouraged, has suffered from the moving of the ARL-Sensors Directorate and from some transfer of their centres of interest as well.

We propose, after discussion with our U.S. partners (Dr. J. Zavada), our collaboration to continue in the framework of an additional contract of one year on two main objectives.

First, at half of the time, the completion of the ZnSe study, according to the above proposals. We would like as well to diversify the growth approach, and to develop the solution growth of ZnSe, using a new solvent we have found out. This could allow to obtain larger twin-free crystals.

Second, we propose to tackle the ZnO growth. ZnO appears as an attractive material as alternative substrate for the growth of GaN epilayers. It shows the same crystallographic structure as GaN with a lattice mismatch less than 1.8%. Because of its large band gap of 3.2 eV, ZnO could further act itself as candidate for blue-emitting devices. Its shear modulus, which has been identified to be a key structural signature of the materials, has been calculated using the semi-empirical law: in spite of the very high ionicity of its chemical bond, ZnO presents the highest shear modulus of the II-VI family, and then the most stable lattice, because of its very small interatomic distance.

In order to grow ZnO crystals, several techniques should be implemented : vapor growth, either using as sublimation activator a H_2-H_2O mixture, that we have found out to be a good sublimation catalyzer, or an halogen for chemical vapor transport ; second, solution growth, using two good solvents that we have found out for ZnO. Concerning the activated sublimation, we have used the technique of close spacing vapour transport (CSVT), allowing fast experiments and easy determination of the growth rate, to determine the thermodynamic constants of the transport from a theoretical model developed in the laboratory.

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